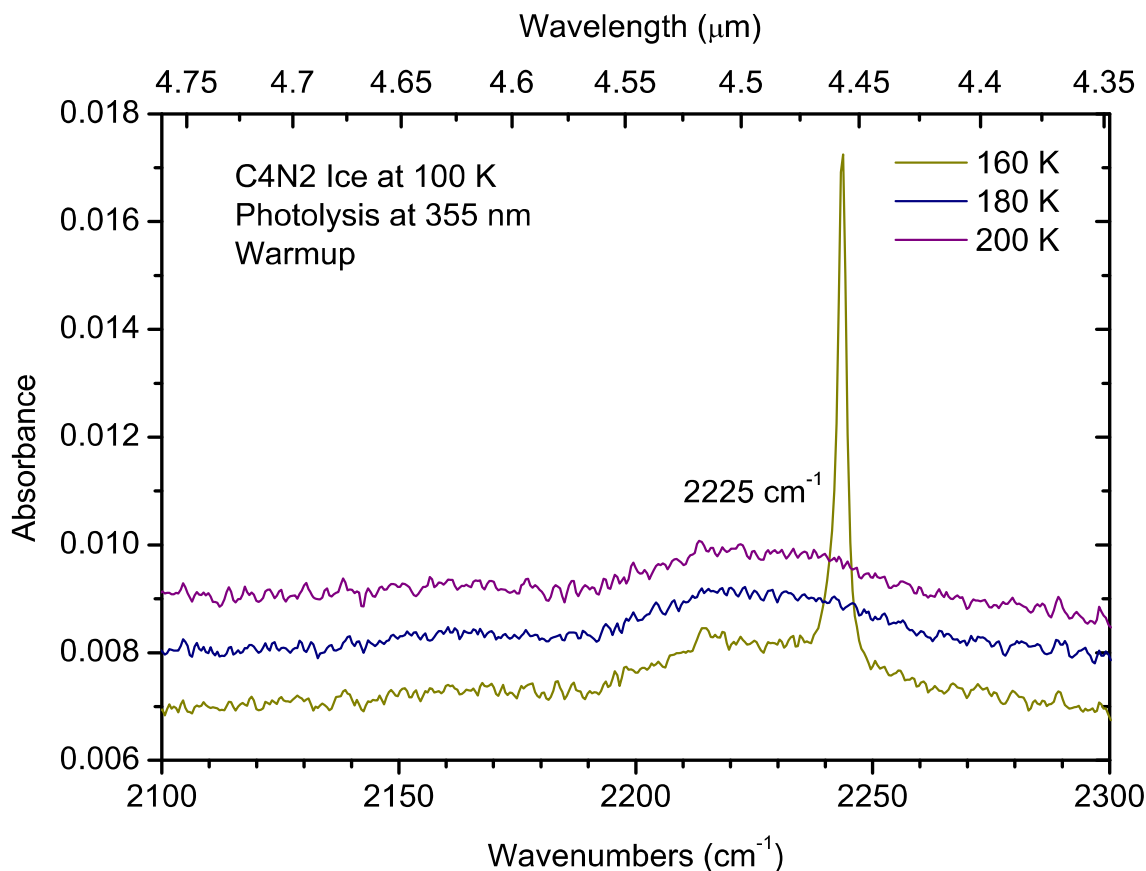


## Supplementary Information

### Photochemical Activity of Titan's Low-Altitude Condensed Haze

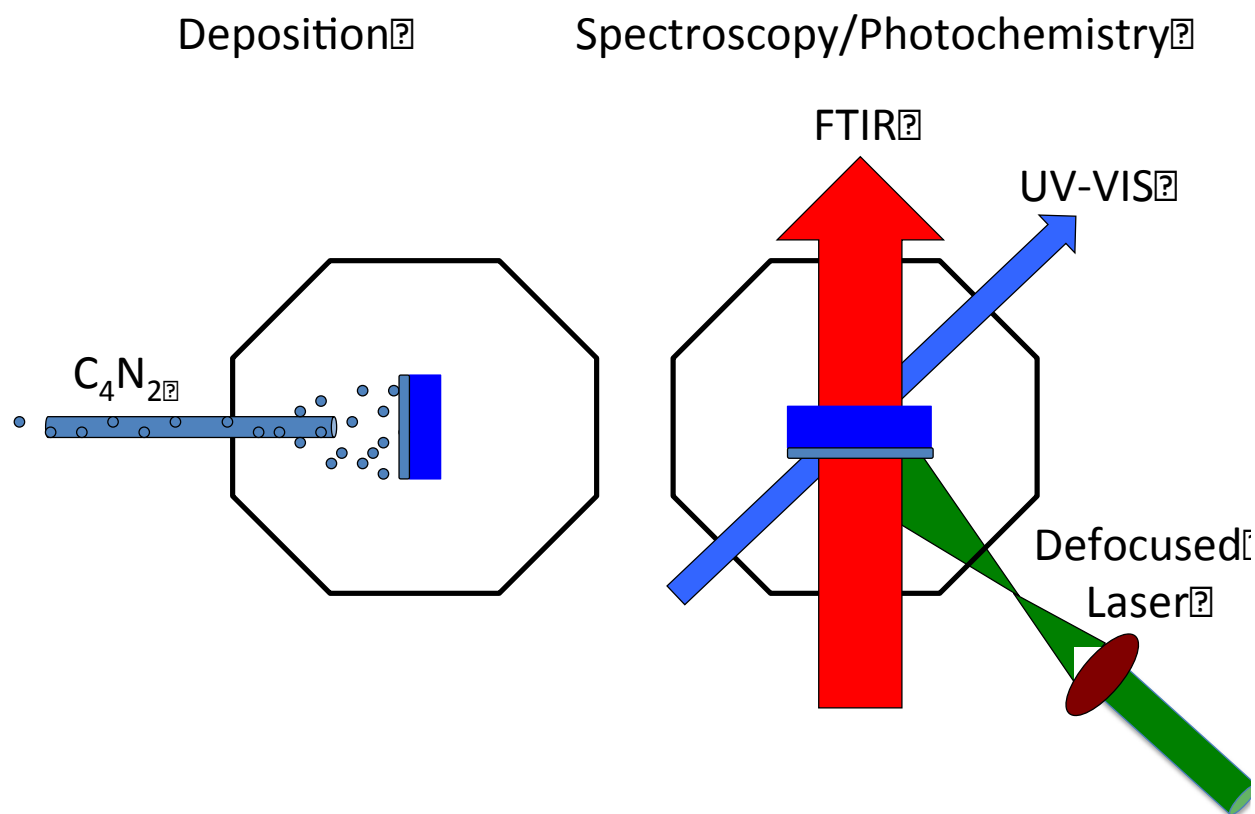
Murthy S. Gudipati<sup>\*1</sup>, Ronen Jacovi<sup>2</sup>, Isabelle Couturier-Tamburelli<sup>3</sup>, Antti Lignell<sup>4</sup>, Mark Allen<sup>1</sup>



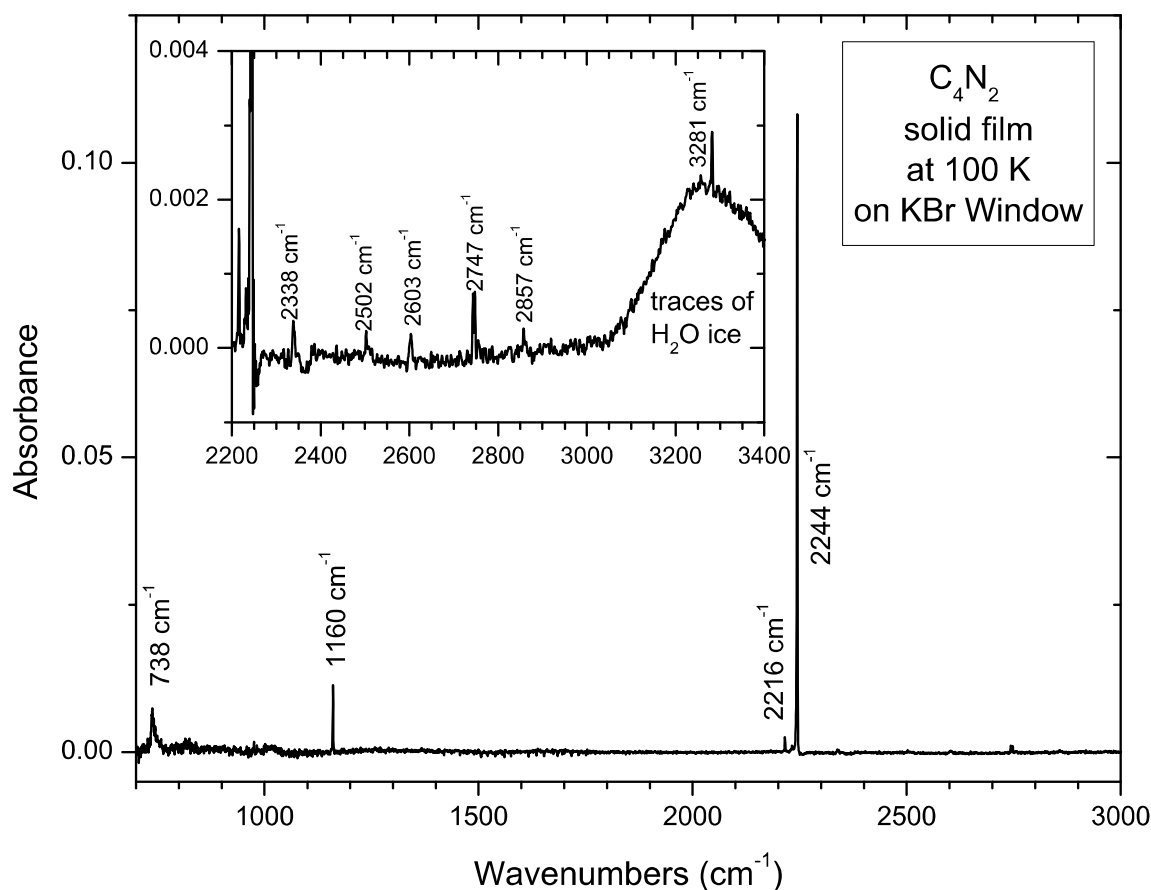
**Supplementary Figure S1: Spectral changes in the infrared during the warm-up of photoprocessed dicyanoacetylene:** Absorption spectra of C<sub>4</sub>N<sub>2</sub> ice film during warm-up subsequent to 355 nm laser photolysis. Small amount of residual C<sub>4</sub>N<sub>2</sub> can still be seen at 160 K through 2244 cm<sup>-1</sup> absorption band, which completely sublimates at 180 K. Remaining broad absorption band centered ~2225 cm<sup>-1</sup> is reminiscent of >300 nm high-pressure Hg lamp photolysis conducted in France (Figure 4 bottom). The broad polymer absorption is clearly seen as a shoulder even at 160 K. At lower temperatures C<sub>4</sub>N<sub>2</sub> absorption itself is so strong that it dominates the surrounding regions.



**Supplementary Figure S2: A photograph of the equipment at JPL used in these studies:** Experimental Set-up to measure simultaneous UV transmission and FTIR spectra of Titan organic ice condensates. The rotatable ice-deposition window is mounted on the tip of a close-cycle Helium cryostat, which can be maintained between 10 and 300 K. In the background right side are the fumehoods that were used to synthesize C<sub>4</sub>N<sub>2</sub>. A -80° C refrigerator in which the C<sub>4</sub>N<sub>2</sub> sample is stored for extended periods can be seen behind the instrument at the top-left corner.



**Supplementary Figure S3: Configuration of the experiments at JPL:** A sketch of the experimental procedure to measure simultaneous UV transmission and FTIR spectra of Titan organic ice condensates.  $C_4N_2$  ice film is deposited first (left). The substrate and sample are rotated to measure UV and IR spectra (right) to monitor sufficient condensation of the sample on the substrate. Subsequently the substrate is fixed in a geometry shown on right that enables laser photolysis and measurement of both UV and IR spectra without rotating the sample position – this procedure ensures highest reproducibility of spectral data during the photolysis experiments.



**Supplementary Figure S4: Infrared spectrum of dicyanoacetylene ice:** Infrared spectrum of  $C_4N_2$  solid film on a KBr substrate at 100 K, enabling detection of spectral features below  $2000\text{ cm}^{-1}$  compared to a Sapphire substrate, which on the other hand has excellent optical quality in the UV-VIS spectral region. In addition to the CN asymmetric stretch at  $2244\text{ cm}^{-1}$ , two more strong absorptions at  $738\text{ cm}^{-1}$  and  $1140\text{ cm}^{-1}$ , and additional combination bands between  $2250$  and  $3400\text{ cm}^{-1}$  can clearly be seen. All these spectral features are observed in isolated  $C_4N_2$  in Ar matrices and assigned [Guennoun, Z., Couturier-Tamburelli, I., Pietri, N., & Aycard, J.P., UV photoisomerisation of cyano and dicyanoacetylene: the first identification of CCNCH and CCCNCN isomers - matrix isolation, infrared and ab initio study. Chemical Physics Letters 368 (5-6), 574-583 (2003)]